SCIENCE FOR GLASS PRODUCTION

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COLOR CONTROL AND REDOX BALANCE MONITORING IN CONTAINER GLASS

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Modern methods and systems for monitoring the redox balance in glass as a key parameter for stabilizing the glassmaking process and attaining reproducible prescribed functional properties of glass and glass articles are examined. It is shown that the value of the trichromatic characteristics — the dominant wavelength, purity, and brightness of the color — must be used to monitor the light protection function of glass.

The market for glass bottles has enormous potential because glass containers are high-quality packing materials, the demand for which is increasing together with the real income of the population. The problems of maintaining, monitoring, and controlling the quality of glass containers will become increasingly more acute with each passing year. One reason for this are two conflicting trends which have appeared in the last few years: on the one hand glass quality the requirements are becoming more stringent while on the other hand ecological norms dictate that secondary products with unstable composition, such as glass scrap, slags, and dust from filters, be used in glassmaking. Glass scrap, often with mixed colors, is already being used in amounts up to 85% to make container glass [1]. Both problems can be successfully solved by adopting innovative glass-production technologies with better and faster process-control systems.

In this connection it is timely to examine methods and systems for monitoring the color characteristics of glass containers and the redox balance of glass.

Glass containers have a number of indisputable qualitative advantages over other forms of packaging — transparency, chemical inertness, safety, the possibility of recycling and salvaging of wastes, and wide selection. Brown and green glass containers have another important characteristic: strong absorption of ultraviolet and short-wavelength visible light, thereby providing long-term biological protection of the contents.

It is known that when exposed to ultraviolet light many beverages (principally, beer) containing carbonic acid lose the aroma, taste, and health qualities for which they are valued. This draws attention, and not only from manufacturers of glass containers, to the protective function of the packaging. For example, the new packaging standard — Pantsir', made of polyethyleneterephthalate (PET) — adopted by "Pivovarennaya kompaniya Balika" OJSC provides good protection for beer from UV radiation. Adding a photoprotective component to the packaging material substantially improves the protective properties of PET. The composition of packaging with enhanced protective properties is an exclusive development achieved by the company and is guarded as a commercial secret. It has been announced that the problem of ideal packaging for beer has essentially been solved, since the new PET container is not only light and convenient for shipping (the tare weight of a half-liter bottle is 28 g) but it also provides reliable protection for the contents.

Domestic manufacturers of glass containers for beer and other beverages containing carbonic acid have probably already encountered or will soon encounter the strict requirements which foreign beer producers now impose on the color (protective) characteristics of bottles.

Thus, Sun Interbrew Company, a Belgian brewery, mandates the use of the RGB color model to determine the trichromatic parameters of glass — the predominate wavelength (background color), the color purity (degree of saturation), and the color brightness (reflectivity factor). The term "trichromatic" is used to describe normal color vision by which humans perceive all three basic colors (red, green, and blue). At the Sun Interbrew Company every bottle is checked and the maximum admissible percentage of noncritical defects must not exceed 0.65.

Such stringent requirements can be met only if bottle manufacturers possess the appropriate monitoring capability.

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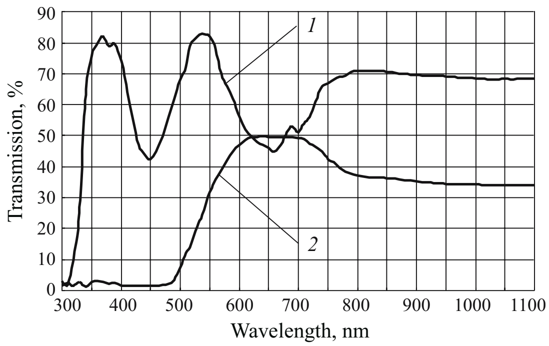

Fig. 1. Transmission spectra of green (*1*) and brown (*2*) container glass.

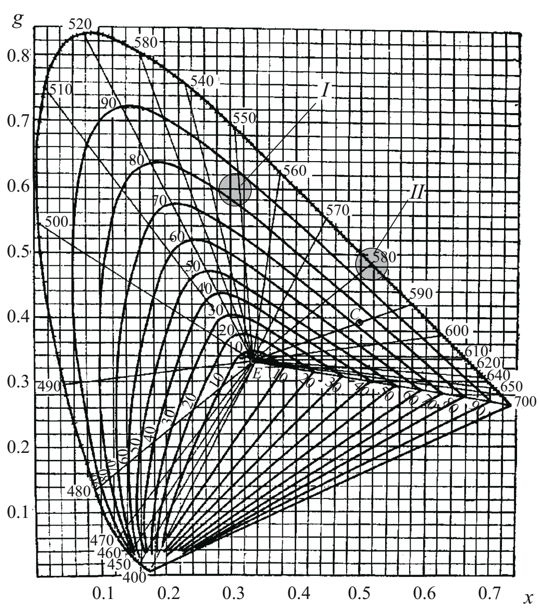

Fig. 2. Arrangement of the color tone regions of green (*I*) and brown (*II*) container glasses in the RGB color diagram.

However, many domestic plants do not even monitor the light transmission of green and brown glass containers even though GOST R 52022–2003 requires that they do so. This is completely inadmissible.

The very large Russian company — "Rusdzham" LLC (Turkey – Russia) — monitors the trichromatic parameters of green and brown containers on a daily basis. Today, "Rusdzham," whose technology and product quality meet the international standards, is the leading producer of glass containers in Russia. Breweries comprise 25% of the Russian market for glass containers; the bottles are SAB Miller, Efes, Sun Intebrew, Heineken, Balika, Vena, and others.

The trichromatic parameters are determined from the optical transmission spectra obtained for green and brown glass in the wavelength range 300 – 1100 nm (Fig. 1) in the RGB coordinate system (Fig. 2). A specially developed program, based on the Hardy – Littlewood number theory method, is used to analyze the spectra [2].

The RGB coordinates of green and brown bottles must correspond exactly to the fields indicated in Fig. 2. According to the technical requirements of "Rusdzham" LLC, the dominant wavelength of green and brown glass must fall within the ranges 552 – 558 nm and 578 – 586 nm, respectively. This guarantees that the bottles will have high protective qualities.

The stability of the technological process as a whole and, first and foremost, the redox state of the glass mass keep the color tone of the glass within the indicated limits. The key parameter that determines the stabilization and reproducibility of the glassmaking process and, therefore, the properties of the glass itself is the oxygen partial pressure in the glass mass [3 – 6].

The chemical composition of the glass, the batch composition, the atmosphere inside the furnace, the heating history of the glass, and other factors determine the oxygen partial pressure.

In turn, the oxygen pressure that is established determines the diverse and complex redox interactions and the equilibrium states of the polyvalent elements in the glass mass, which contains iron oxides, carbon, and sulfur:

$$C + CO_2\ (\text{gas}) \rightarrow 2CO\ (\text{gas});$$

$$2Fe^{3+} + O^{2-} + CO\ (\text{gas}) \rightleftarrows 2Fe^{2+} + CO_2\ (\text{gas});$$

$$SO_4^{2-} + CO\ (\text{gas}) \rightleftarrows SO_2\ (\text{gas}) + CO_2\ (\text{gas}) + O^{2-};$$

$$2SO_4^{2-} + 6CO\ (\text{gas}) \rightleftarrows S_2\ (\text{gas}) + 6CO_2\ (\text{gas}) + 2O^{2-};$$

$$SO_4^{2-} + 4CO\ (\text{gas}) \rightleftarrows S^{2-} + 4CO_2\ (\text{gas});$$

$$SO_4^{2-} \rightleftarrows SO_2 + O^{2-} + SO_2;$$

$$S^{2-} + 3SO_4^{2-} \rightleftarrows 4SO_2 + 4O^{2-};$$

$$3S^{2-} + SO_4^{2-} \rightleftarrows 2S_2 + 4O^{2-};$$

$$SO_4^{2-} + 8Fe^{2+} \rightleftarrows S^{2-} + 8Fe^{3+} + 4O^{2-}.$$

The equilibria which are established give rise to fundamental processes such as radiative heat transfer, fining and foaming, decolorization, and tinting.

High-quality fining of the glass mass is important in the production of any type of glass. The duration and the degree of fining are determined directly by the amount of SO_3 lost in the melting process. The solubility of SO_3 in the glass mass is a function of the oxygen partial pressure (Fig. 3) [5]. Oxidized glasses contain more and reduced glasses less SO_3, the latter being finer. Thus, the search for rational conditions for high-quality fining must be based on the redox balance in the glass mass, and the problem must be solved separately in each individual case.

Variable-valence elements — chromium, iron, sulfur, and carbon — are present in green and brown container glasses and a redox equilibrium must be established between them during melting, thereby imparting the required color to the glass and the required degree of protection. For example,

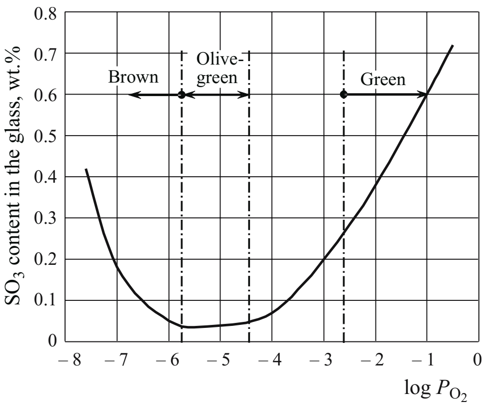

Fig. 3. Solubility of SO_3 in the glass mass as a function of the oxygen partial pressure (P_{O_2}, atm).

the amber chromophore $[Fe^{3+}O_3S^{2-}]^{5-}$ is a structural group consisting of a tetrahedrally coordinated Fe^{3+} ion surrounded by one sulfide sulfur ion and three oxygen ligands. Of course, there exists a region of redox states of the glass mass that determines the formation of the required amount of amber chromophore, since a melt in the oxidized state will contain too much Fe^{3+} and too little sulfide sulfur and a melt in the reduced state will contain too little Fe^{3+} and excess sulfide.

This complex chain of intercoupled, interdependent, technology-determining phenomena and processes forms the basis of a serious approach to the problem of monitoring and stabilizing the oxidation-reduction (redox) state of the glass mass at a prescribed level.

In domestic commercial glassmaking redox monitoring is performed, in the best case, by periodically measuring the properties of finished articles — the color (transmission spectra), the sulfur content (chemical analysis), and the ratio of the forms of iron with different valence (chemical or spectral analysis).

An effective redox monitoring method is to evaluate the oxidation-reduction potential (ORP) of the batch by means of the Simpson indices. The Simpson indices of the raw materials have been determined experimentally [7 – 9]. The reducing agents in glass batches include carbon, anthracite, iron pyrites, iron chromite, and slags with indices ranging from – 0.10 to – 9.00. The oxidizing agents include sodium sulfate, cerium and iron oxides, and sodium and potassium nitrates with indices ranging from + 0.19 to + 1.20.

It is very important to maintain the optimal batch ORP, which ensures that the glass-making process will be stable and the product will have the prescribed color (protective) characteristics and high quality. The specialists at "Rusdzham" LLC use the ORP as a starting parameter for developing the batch composition (including a slag batch), especially for adjusting the quantity of oxidizing and reducing agents, reproducing the melting conditions in different glass-melting furnaces, and developing a regime for changing the color of the glass mass in the furnace. It is considered effective to maintain the ORP at the level – 15 ... – 20 for emerald green glass and – 25 ... – 30 for brown glass, and the ORP of the batch for colorless glass should lie in the range from + 5 to + 20.

Fig. 4. Arrangement of the oxygen sensors in a commercial furnace used for making container glass: *1*, *2*) batch and feeder sensors, respectively.

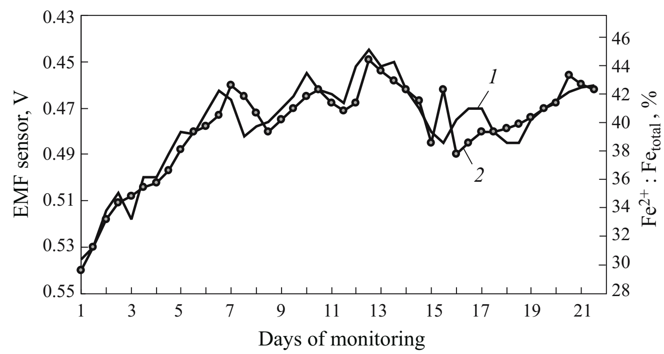

Fig. 5. Correlation between the signal from the oxygen sensor placed in the feeder (*1*) and the ratio Fe^{2+} : Fe_{total} in the glass mass (*2*).

The ORP values presented in each concrete case can be adjusted somewhat depending on the chemical need for oxygen of the raw material and glass scrap used or in connection with a change in the redox function of the glass-melting furnace.

This simple and quite effective redox monitoring method is ignored in most Russian glass manufacturing plants. Our experience in evaluating the ORP of batches for container and medical glasses at different plants shows that there is a large variance in the value of this indicator and at many plants it is far from the recommended level.

The redox monitoring methods used are imperfect from the standpoint of the current technical level of container-glass production. They are periodic, are used off-line, and do not permit making the appropriate adjustments in the batch composition promptly so as to maintain the process flow and the product quality at the proper level.

A great deal of attention has been devoted abroad to solving this problem in the last few years — in Germany, the Netherlands, and Belgium [10 – 12]. Specialists have proposed and implemented a method of continual (on-line) monitoring of the redox state of the glass mass. The oxygen concentration is measured by an electrochemical method using oxygen sensors placed inside the glass mass in the batch zone and in the feeder (Fig. 4). It was found that when operating a commercial furnace for the production of green container glass (the production rate is 180 tons/day, batch : scrap =

15 : 85) the maximum cross-correlation between the signals from the sensors in the batch and feeder was reached after 9 h, which corresponded to the process flow rate. A very good correlation was observed between the signals from the sensors in the feeder and the degree of oxidation of the iron in the glass mass (Fig. 5).

In this way the state of the glass mass can be predicted 9 h in advance according to the signal from the batch sensor. When redox "perturbations" of the batch entering the furnace occurred, rapid adjustment of the batch composition made it possible to reduce the color variations in the finished product by a factor of 10 from the initial perturbation.

The on-line adjustment systems are to be implemented by using a combination of hoppers with batches whose redox parameters are different. For example, a furnace in which primarily secondary scrap is used can be equipped with two hoppers containing batches with different ORPs. When scrap with an unstable ORP (mixed color or varying amounts of organic impurities) is used, a choice as two which batch is to be used is made on the basis of the indications of the batch sensor. This is now an entirely real aspect of production, which must be taken into account at the time the furnaces and the systems for feeding batch mixtures and glass scrap are being designed [12].

For Russian glassmaking plants, the optimal solution to the problem of on-line monitoring of the redox state of the glass mass and the color of the glass is an automated system operating in real-time according to the scheme shown below.

Scheme of an automated system for monitoring and controlling the redox balance and color of container glass

Monitoring the initial redox parameters of the batch

Total Fe_xO_y content
FeO : Fe_xO_y ratio
SO_3 content
Carbon content
} **ORP**

↓

Monitoring and stabilization of the redox parameters of the glass mass

O_2 partial pressure
Fe^{2+} : (Fe^{2+} + Fe^{3+}) ratio
Amount of dissolved SO_3

↓

Monitoring of the trichromatic parameters of glass

Predominate wavelength, nm
Color purity and brightness, %

Such systems have already been implemented in commercial glassmaking abroad [11, 12] and are also being used to teach operators how to operate glassmaking furnaces. The initial redox parameters (the total amount of iron oxides and the content of chromium oxide and sodium sulfate in the glass), the oxygen partial pressure in the melt measured by electrochemical sensors, and the established redox equilibria as well as the trichromatic characteristics of the glass computed in real-time are all displayed on the screen of a computer monitor.

More than 30 licensed brands of beer produced by practically all of the large companies in the world are marketed in Russia. Under such conditions the work on increasing packaging quality will only intensify with each passing year. The drive to produce competitive glass bottles should stimulate innovative work, especially in the direction which we have examined.

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